Highlights from Recent Literature

1 Analytical

1.1 Reductive Determination of Gold at a Carbon Paste Electrode using Constant-Current Stripping Analysis

Gold in soil samples has been determined at a carbon paste electrode with tricresyl phosphate using constant-current stripping analysis. J. Konvalina and K. Vytras, Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Czech Republic, *Chem. Listy*, 2001, **95**(8), 505-508, report how gold was accumulated at a potential of +800 mV as tetrachloroaurate and then reduced at a constant current (-3 µA) to Au(0). The interference of Fe(III) present in mineralized samples in large excess was overcome by addition of a fluoride to the measured solution. The standard addition method was used to evaluate unknown concentrations. Precision of the method was checked by determination of recovery of gold spiked into the real matrix. A comparison of the results with those obtained by AAS showed no statistically significant differences.

1.2 Use of p-Sulfobenzylidene Rhodanine as a Colour Developer for the Spectrophotometric Determination of Gold

Y. Yang, Y. Su and G. Li of the Kunming University of Science and Engineering, Kunming, P.R. China, *Huangjin*, 2001, **22**(4), 44-45, have studied the colour development reaction between Au(III) and p-sulfobenzylidene rhodanine (SBDR). A stable red complex (SBDR:Au 2:1) formed in acid medium in the presence of sodium dodecyl benzenesulfonate surfactant. The effects of medium acidity, addition of surfactant and SBDR, and coexistent ions on the reaction were determined. The maximum adsorption wavelength of the complex was at 530 nm, and the mol absorptivity was 6.55×10^4 L $(mol.cm)^{-1}$. Beer's law was obeyed at 0-50 µg ml^{-1}. The method can be used to determine the gold content in wastewater.

2 Catalysis

2.1 Homogeneous Gold-Catalysed Phenol Synthesis

A number of late transition metals with d^8 configuration have been shown to catalyse the formation of a phenol from a suitably substituted alkyne. Gold(III) is however the most active amongst the gold(III), palladium(II), platinum(II), rhodium(I) and iridium(I) systems investigated to date and gold gives the cleanest conversion. A.S.K. Hashmi, T.M. Frost and J.W. Bats of the Institute for Organic Chemistry, University of Stuttgart, *Org. Lett.*, 2001, **3**(23), 3769 - 3771 have demonstrated that the mechanism involves intramolecular transfer of an oxygen atom.

2.2 Electrocatalytic Oxidation of Formaldehyde on Gold

The electrocatalytic oxidation of normal formaldehyde (HCHO) and deuterated formaldehyde (DCDO) was studied on gold in aqueous alkali solution as a function of pH, concentration, potential, and temperature by voltammetry, chronoamperometry, and differential electrochemical mass spectrometry (M.V. ten Kortenaar, Z.I. Kolar, J.J.M. De Goeij and G. Frens, Department of Radiochemistry, Interfaculty Reactor Institute, and Laboratory of Physical Chemistry, Faculty of Applied Sciences, Delft University of Technology, The Netherlands, *J. Electrochem. Soc.*, 2001, **148**(8), E327-E335). The H_2, D_2, and CO_2 gas evolution kinetics depend to a great extent on the pH, potential, and temperature but play only a minor role in the overall rate of the electrooxidation reaction. The evolution of hydrogen at the open-circuit potential and the current efficiencies larger than 100% pointed toward the occurrence of a non-electrochemical dehydrogenation reaction parallel to the electrooxidation. The kinetic isotope effects and activation energies suggested that the overall rate of the electrooxidation reaction is determined by the hydroxyl-catalysed, enthalpy-driven, chemisorption of the enolate anion at low potentials, by the entropy-driven desorption of the formate anion at higher potentials, and by diffusion at the highest potentials. The apparent activation energies (E_a) ranged in value between -25 and 60 kJ mol^{-1} confirming the highly catalytic properties of gold in determining the overall rate of the reaction. See also L.D. Burke and P.F. Nugent, *Gold Bull.*, 1997, **30**, 43 - 53; 1998, **31**, 39 - 50 and L.D. Burke, A.J. Ahern and A.P. O'Mullane, *Gold Bull.*, 2002, **35**, 3 - 10 : this issue.

2.3 Effect of Gold Promotion on the Reduction Behaviour of Cobalt Supported Catalysts for 1,4-Butanediol Transformation

The reduction behaviour and the catalytic activity in the cyclodehydration of 1,4-butanediol into 2,3-dihydrofuran over a gold promoted cobalt catalyst have been studied. A.E. Lebedev, L.J. Leite, V.V. Stonkus, L.I. Ilieva, D.Ch. Andreeva and T.T. Tabakova, Latvian Institute of Organic Synthesis, Riga, *Bulg. Chem. Commun.* 2001, **33**(2), 148-155, have shown that modification of the supported cobalt catalyst with gold leads to the formation of new cobalt species which are reduced at significantly lower temperatures than the non-promoted catalyst.

2.4 Gold-Based Mono- and Bimetallic Nanoparticles on HY Zeolites

Stable nanoparticles of monometallic gold, or bimetallic Pd-Au and Pt-Au systems supported on Y-zeolite were obtained by G. Riahi, D. Guillemot, M. Polisset-Thfoin, D. Bonnin and J. Fraissard, SIEN - ESA 7069, Université Paris VI, France, *Stud. Surf. Sci. Catal.*, 2001, **135** (Zeolites and Mesoporous Materials at the Dawn of the 21st Century), 1594-1601, using an original method. The metallic precursors and the support play an important part in the formation and the stability of the particles. This method involves exchange of complexed cations with counter-ions of an acidified zeolite and their thermal reduction by the ligand (ethylenediamine) under inert gas flow. This preparation leads to nanometric mixed bimetallic particles. The particles have good stability at high temperature (500°C) in dihydrogen or dioxygen.

2.5 Method of Regenerating Ultrafine Gold Particle Catalyst

This patented process (M. Date, Y. Ichihashi and M. Haruta, Ministry of Economy, Trade and Industry, National Industrial Research Institute, Japan, Japanese Patent 2001334155 A2, 4 Dec 2001) consists of irradiating a catalyst *(eg* Au/TiO_2) having reduced catalytic activity with light corresponding to an absorption band of the catalyst in the presence of oxygen. The process is able to reactivate the catalyst at room temperature using irradiation by light.

2.6 Activity, Selectivity, and Long-Term Stability of Different Metal Oxide Supported Gold Catalysts for Preferential CO Oxidation in Hydrogen-Rich Gas

A comparative study of the catalytic performance and long-term stability of various metal oxide supported gold catalysts during preferential CO oxidation at 80°C in a hydrogen-containing atmosphere (PROX) reveals significant support effects (M.M. Schubert, V. Plzak, J. Garche and R.J. Behm, Abteilung Oberflachenchemie und Katalyse, Universität Ulm, Germany, *Catal. Lett.*, 2001, **76**(3-4), 143-150). Compared with $Au/\gamma\text{-}Al_2O_3$, where the support is believed to behave neutrally in the reaction process, catalysts supported on reducible transition metal oxides, such as Fe_2O_3, CeO_2, or TiO_2, exhibit a CO oxidation activity of up to one magnitude higher at comparable gold particle sizes. The selectivity is also found to strongly depend on the metal oxide employed, amounting, *eg*, up to 75% for Au/Co_3O_4 and down to 35% over Au/SnO_2. The deactivation, which is observed for all samples with increasing time on stream, except for $Au/\gamma\text{-}Al_2O_3$, is related to the build-up of surface carbonate species. The long-term stability of the investigated catalysts in simulated methanol reformate depends crucially on whether or not such by-products are formed, with magnesia and Co_3O_4 supported catalysts being deactivated the most. Overall, Au/CeO_2 and, in particular, $Au/\alpha\text{-}Fe_2O_3$ represent the best compromise under the applied reaction conditions, especially due to the superior activity and the easily reversible deactivation of the latter catalyst.

2.7 Synthesis of Symmetric Ureas by Oxidative Carbonylation of Amines over Resin-Immobilized Gold

Symmetric ureas were synthesized with high efficiency and selectivity by oxidative carbonylation of aromatic and aliphatic amines in the presence of resin immobilized gold, and 99% selectivity was achieved when using aniline as the substrate. In work described by F. Shi, Y.-Q. Deng, C.-K. Gong, T.-L. Sima and H.-Z. Yang, of the State Key Laboratory Oxo Synthesis Selective Oxidation, Lanzhou Institute of Chemical Physics, The Chinese Academy Sciences, P.R. China, *Huaxue Xuebao*, 2001, **59**(8), 1330-1334, no other organic solvent was used in the reactions and highly pure products could be obtained due to the high selectivity and the easy separation of the catalyst from the reaction system.

2.8 Catalytic Performance and Structural Characterization of Ferric Oxide Supported Gold

Z. Hao, L. An and H. Wang of the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, P.R. China, *Science in China, Series B: Chemistry*, 2001, **44**(6), 596-605, have studied the preparation and catalytic activity of gold catalysts having ferric oxide and its composite oxides as supports for low-temperature CO oxidation, and characterized extensively by XRD, XPS, TPR, EC and XAFS techniques. It was found that highly dispersed nanoparticles of partially oxidized gold supported on Fe_2O_3 and $NiFe_2O_4$ had high catalytic activity at low temperatures.

2.9 Use of Low Frequency Raman Modes for Gold Nanocluster Size Measurement in Catalytic Beds

Low frequency Raman (LFR) modes have recently been used by R.S. Cataliotti, A. Morresi, M. Ombelli and G. Compagnini, Dipartimento di Chimica, Laboratorio di Chimica Fisica, Universita di Perugia, Italy, *Materials Science & Engineering, C: Biomimetic and Supramolecular Systems*, 2002, **C19**(1-2), 181-184, to determine the size of nanoparticles of silver and gold. This has now been used to measure the sizes of gold particles embedded in two differently prepared cerium oxides whose activities were found to be quite different in the oxidation reactions.

2.10 Preparation of Gold Nanoparticles in Inorganic Suspension and Clay Gel

Gold nanoparticles have been prepared in titania, silica and clay suspensions by reduction of tetrachloroauric ions (K. Nakamura and Y. Mori, Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Japan, *Journal of Chemical Engineering of Japan,* 2001, **34**(12), 1538-1544). The formation rates of gold nanoparticles in titania and silica suspensions were almost the same as that in an aqueous solution. Slower formation rates were obtained in a clay gel solution, becoming slower with increasing clay concentration. Although the gold nanoparticles became large and polydispersed, due to the slow diffusion rate of tetrachloroauric ions in the clay gel, the good dispersion of gold nanoparticles was retained even after the clay gel had dried.

3 Chemistry

3.1 Synthesis of Tetramethylammonium Auride

Using a macroreticular ion exchange resin with a high affinity towards caesium ions in liquid ammonia, P.D.C. Dietzel and M. Jansen, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany, *Chem. Commun*., Cambridge, 2001, (21) 2208-2209, have prepared tetramethylammonium auride, the first compound of negatively charged gold with a non-metal cation. This compound is isostructural with the corresponding bromide which illustrates again the similarities between gold and the halogens.

3.2 Synthesis of a Large Water-Soluble Gold Cluster (Au_{32-36}) and its Properties as a Potential Label in Electron Microscopy

A water-soluble gold cluster with a core of 32 to 36 gold atoms has been prepared using $NaBH_4$ reduction of the AuCN complex of n-butylbis(5-morpholinocarbonyl-2-furyl)phosphine and characterized by its mass spectrum. W. Jahn of the Max-Planck-Institut für Medizinische Forschung, Abteilung Biophysik, Heidelberg, Germany, Z. *Naturforsch., B: Chem. Sci*., 2001, **56**(8), 728-734, has studied the chromatographic behaviour, ligand exchange and binding to actin.

3.3 Polymers, Rings and Oligomers Containing Gold(I) Centres

R.J. Puddephatt of the Department of Chemistry, The University of Western Ontario, London, ON, N6A 5B7, Canada, *Coord. Chem. Rev*., 2001, **216-217**, 313-332, has written a review on this topic, with 28 references, in which current research on the synthesis of macromolecules containing linear Au(I) centres is discussed. These polymers range from conjugated, rigid-rod polymers to macrocyclic compounds, including novel catenanes and a doubly braided catenane formed in high yield by simple self assembly.

4 Coatings, Films, Membranes and Wires

4.1 Multi-Shell Gold Nanowires under Compression

The deformation properties of multi-wall gold nanowires under compressive loading have been studied by G. Bilalbegovic, Department of Physics, University of Rijeka, Croatia, *Los Alamos Natl. Lab., Prepr. Arch., Condens. Matter*, 4 Oct. 2001, 1-14. Nanowires were simulated by using a realistic many-body potential. Simulations start from cylindrical fcc(111) structures at 0 K. After annealing cycles, axial compression is applied to multi-shell nanowires having a number of radii and lengths at 300 K. Several types of deformation are found, such as large buckling distortions and progressive crushing. Compressed nanowires recover their initial lengths and radii even after severe structural deformation. However, in contrast to carbon nanotubes irreversible local atomic rearrangements occur even under small compressive strains.

4.2 Gold-Nanocluster-Doped Inorganic-Organic Hybrid Coatings on Polycarbonate and Isolation of Shaped Gold Microcrystals from the Coating Sol

Gold-nanocluster-doped inorganic-organic hybrid coatings were prepared on polycarbonate substrates for application as abrasion-resistant coloured coatings as well as nonlinear optical material. G. De and D. Kundu of the Sol-Gel Division, Central Glass and Ceramic Research Institute, Jadavpur Kolkata, India, *Chemistry of Materials*, 2001, **13**(11), 4239-4246, have shown that the gold-doped sol was prepared by incorporating $HAuCl_4.4H_2O$ into a composite sol derived from 3-(glycidoxypropyl)trimethoxysilane, tetraethylorthosilicate, and 3-(methacryloxypropyl) trimethoxysilane *via* hydrolysis-condensation and epoxy polymerization reactions. When the coated substrates were exposed under UV light, three reactions occurred simultaneously: (i) reduction of gold ions into metallic gold nanoclusters, (ii) polymerization of methacrylate groups, and (iii) strengthening of the silica network. As a result, the UV-cured coatings became reddish-purple and more abrasion-resistant than the polycarbonate substrate. UV-vis spectroscopy and TEM of the films showed a peak at 530 nm due to the surface plasmon resonance of the gold nanoclusters and the presence of 8-10 nm spherical gold nanoclusters, respectively. XRD of the films also showed the characteristic peaks of metallic gold nanoclusters. The inorganic-organic hybrid network at the sol stage also acted as a new breeding medium for the generation of shaped (triangular, hexagonal, prismatic, *etc*) gold microcrystals from the gold-doped sol without UV irradiation. Electron diffraction suggests that these were single crystals with a preferential growth along the Au (111) plane.

5 Colloids and Nanotechnology

5.1 Optical Properties of Gold and Silver Nanoclusters Investigated by Liquid Chromatography

J.P. Wilcoxon, J.E. Martin and P. Provencio of the Nanostructures and Advanced Materials Chemistry Department, Sandia National Laboratories, Albuquerque, NM, USA, *J. Chem. Phys*. 2001, **115**(2), 998-1008, have reported HPLC and TEM studies of the size-dependent absorbance properties of gold and silver nanoclusters dispersed in organic solvents. These nanosize metal clusters were synthesized by an inverse micelle synthetic technique at room temperature in inert oils and those studied range in diameter from 1.3-8 nm. HPLC allowed the separation of the clusters from all other chemicals and size select to a resolution of ±2 Å. The authors used an online photodiode array to study the size-dependent absorbance properties of these clusters. For both Au and Ag clusters in the size range 8 to 1.5 nm, the plasmon line width broadens following a 1/R linewidth size dependence whose slope is greatest for gold. The peak asymmetry in the plasmon band shape is greatest for gold and increases with decreasing size for both Au and Ag clusters. The plasmon peak energy blue shifts with decreasing size for Au clusters while in the case of Ag nanoclusters a red shift is observed.

5.2 Formation of Gold Colloids using Thioether Derivatives as Stabilizing Ligands

Thioethers were used by X.M. Li, M.R. de Jong, K. Inoue, S. Shinkai, J. Huskens and D.N. Reinhoudt of the Laboratory of Supramolecular Chemistry and Technology, MESA Research Institute, University of Twente, Enschede, The Netherlands, *J. Mater. Chem*., 2001, **11**(7), 1919-1923, as adsorbates for preparing gold nanoparticles. Different thioether derivatives having one to four thioether functionalities were synthesized. Colloids were prepared in a two-phase system, and characterized by ^{1}H NMR and TEM. The stability of colloids protected by thioethers increases with the number of ligands per molecule. Monothioethers need longer chain lengths or costabilization by $(oct)_4NBr$ to give stable, redispersible gold colloids. Gold colloids stabilized by the bis(thioether) 5 could not be redispersed after precipitation. Colloids stabilized by the tris(thioether) 6 were only formed at elevated temperature (60°C) indicating the need for chain reorientation to attain stable colloids. Tris(thioether) 7 gave stable colloids at room temperature, which could be redispersed even after precipitation. Tetrakis(thioether) 8 gave the smallest particle size and narrowest size distribution.

5.3 Controlling the Transport Properties of Gold Nanotubule Membranes Using Chemisorbed Thiols

S.B. Lee and C.R. Martin, Department of Chemistry and Center for Chemical Research at the Bio/Nano Interface, University of Florida, Gainesville, USA, *Chem. Mater*., 2001, **13**(10), 3236-3244, have developed a new class of synthetic membranes that consist of a porous polymeric support that contains an ensemble of gold nanotubules that span the complete thickness of the support membrane. The support is a commercially available microporous polycarbonate filter with cylindrical nanoscopic pores. The gold nanotubules are prepared via electroless deposition of gold onto the pore walls; *ie*, the pores act as templates for the nanotubules. By controlling the gold deposition time, Au nanotubules that have effective inside diameters of molecular dimensions (<1 nm) can be prepared. Hence, these membranes are a new class of molecular sieves. In addition, because the tubules are composed of gold, known Au-thiol chemistry can be used to change the chemical environment within the tubules.

This paper reviews recent research on using chemisorbed thiols to control the transport properties of gold nanotubule membranes. The use of both electrically neutral thiols to introduce chemical-transport selectivity and charged thiols to introduce ion-transport selectivity is reviewed.

5.4 Seeding Growth for Size Control of 5-40 nm Diameter Gold Nanoparticles

Following a seeding growth approach, gold nanoparticles of diameters 5-40 nm were prepared with 10-15% standard deviation in diameter from 3.5 ± 0.7 nm gold particle seeds (N.R. Jana, L. Gearheart and C.J. Murphy, Department of Chemistry and Biochemistry, University of South Carolina, Columbia, USA, *Langmuir*, 2001, **17**(22), 6782-6786). Particle size can be controlled by varying the ratio of seed to metal salt, and thus any size in the range 5-40 nm can be prepared. The method can also be scaled up to produce 10-100 mg of gold nanoparticles.

5.5 Preparation of Gold Nanoparticles in the Presence of Dendrimers with Surface Methyl Ester Groups

K. Esumi, A. Kameo, A. Suzuki and K. Torigoe, Department of Applied Chemistry and Institute of Colloid and Interface Science, Science University of Tokyo, Japan, *Colloids Surf., A*, 2001, **189**(1-3), 155-161, have prepared gold nanoparticles by reduction of $HAuCl_4$ with $NaBH_4$ in the presence of poly(amidoamine)dendrimers with surface methyl ester groups in formamide or DMF. Although solutions of $HAuCl_4$ in formamide, in the presence of the dendrimers, were already reduced to some extent, the addition of $NaBH_4$ provided gold nanoparticles whose size decreased with an increase of the

dendrimer generation as well as with the concentration of the dendrimers. However, gold nanoparticles prepared in DMF in the presence of the dendrimer were highly monodispersed. In addition, the authors discussed how the dendrimers acted as templates for the preparation of gold nanoparticles (see also O. Rossell, M. Seco, A.-M. Caminade and J.-P. Majoral, *Gold Bull.*, 2001, **34**, 88 - 94).

5.6 Nonlinear Optical Properties in Three Novel Nanocomposites with Gold Nanoparticles

The nonlinear optical properties of three novel nanocomposites with zerovalent noble metal gold nanoparticles have been studied by S. Qu, Y. Song, C. Du, Y. Wang, Y. Gao, S. Liu, Y. Li and D. Zhu, Department of Physics, Harbin Institute of Technology, P.R. China, *Opt. Commun.*, 2001, **196**(1-6), 317-323, using a Z-scan technique. Optical limiting effects were measured with 8 ns pulses at 532 nm. The cross-sections of nonlinear absorption were obtained by the simulation with a simplified model in which the effective excited-state absorptions of three ligands in nanocomposites were considered. The nonlinear refractive indices were calculated from the data of Z-scan measurement. The experimental results are significantly different in these nanocomposites. Optical nonlinearities can be attributed to the strong excited-state absorptions of the ligands and the surface plasmon resonance of the gold nanoparticles.

5.7 Site-Specific Attachment of Gold Nanoparticles to DNA Templates

DNA was used as a scaffold for the binding of gold nanoparticles using a standard chemical technique. K.A. Stevenson, G. Muralidharan, L. Maya, J.C. Wells, J. Barhen and T. Thundat, Life Sciences Division, Oak Ridge National Laboratory, TN, USA, *Mater. Res. Soc. Symp. Proc.*, 2001, **635**(Anisotropic Nanoparticles), C4.2/1-C4.2/4, have designed a DNA template with amino-modified thymines located every 3.7 nm, which would allow the attachment of the carboxylic acid functionalized gold nanoparticles. The gold particles were covalently bound to the amino groups on the DNA using standard 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) in the presence of a competitor to block excess gold binding sites. The products were analysed by TEM microscopy and atomic force microscopy.

5.8 Gold Nanoparticle Single-Electron Transistor with Carbon Nanotube Leads

Carbon nanotubes have been made to contact a 7 nm gold particle by scanning-probe manipulation (C. Thelander, M.H. Magnusson, K. Deppert, L. Samuelson, P.R. Poulsen, J. Nygard and J. Borggreen, Solid State Physics/Nanometer Consortium, Lund University, Sweden, *Appl. Phys. Lett.*, 2001, **79**(13), 2106-2108). The result was a single-electron transistor showing a periodic modulation of the current as a function of gate voltage for temperatures up to *ca* 200 K, with the particle responsible for the main features of the electron transport. This interpretation could be verified when the particle was removed and the two nanotubes were moved into electrical contact.

5.9 Heat-Induced Size Evolution of Gold Nanoparticles in the Solid State

T. Teranishi, S. Hasegawa, T. Shimizu and and M. Miyake of the School of Materials Science, Japan Advanced Institute of Science and Technology, Ishikawa, Japan, *Advanced Materials*, (Weinheim, Germany), 2001, **13**(22), 1699-1701, have described a simple and useful method to manipulate the size of gold nanoparticles using heat treatment in the solid state. The size of the gold nanoparticles could be controlled from 3 to 10 nm by changing the temperature of the heat treatment (150 - 250°C) and/or the stabilizing agent (tetraoctylammonium bromide). Then self-assembled 2D superlattices of size-controlled gold nanoparticles were fabricated with completely hexagonal packing.

5.10 Bioreduction of $AuCl^{4-}$ Ions by the Fungus, Verticillium sp and Surface Trapping of the Gold Nanoparticles Formed

The bioreduction of aqueous $AuCl^{4-}$ ions by the fungus *Verticillium sp.* has been demonstrated by P. Mukherjee, A. Ahmad, D. Mandal, S. Senapati, S.R. Sainkar, M.I Khan, R. Ramani, R. Parischa, P.V. Ajayakumar, M. Alam, M. Sastry and R. Kumar, Catalysis Division, National Chemical Laboratory, Pune, India, *Angew. Chem., Int. Ed.*, 2001, **40**(19), 3585-3588, to occur on the surface of the mycelia as well as on the cytoplasmic membrane leading to the formation of gold nanoparticles of fairly well-defined dimensions and good monodispersity. The nanoparticles are bound to the surface of the fungal cells and may be used for applications including catalysis and as precursor for the synthesis of coatings for electronic applications. The shift from bacteria to fungi as a means of developing natural nano-factories has the added advantage that processing and handling of the biomass would be much simpler with high productivity.

6 Electrochemistry

6.1 Preparation of 18K Gold Electroplating Bath and Gold Recovery from Plating-Bath Waste

An 18K gold coating has been obtained by S. Li, F. Wu and M. Zhan, Jiaying University, Meizhou, P.R. China, *Huangjin*, 2001, **22**(5), 50-52, using a bath containing gold citrate 5-7 (as Au), Cu EDTA complex 0.5-1 (as Cu), $NiSO_4.6H_2O$ 0.1, $(NH_4)_3C_6H_5O_7$ 100-120, and $H_3C_6H_5O_7$ 20-25 g/L at pH 5.8-6.2, 30 - 35°C, and 0.8-1.2 A/dm^2. The recycling of gold from the waste plating solution and the refining of gold were also discussed.

6.2 Electroless Gold Plating Process

An electroless gold plating process is carried out between room temperature and 80°C in a bath whose pH is 2.0-5.0 (Y. Sato, K. Nomiya and K. Shinbo, Tanaka Noble Metal Industrial Co., Ltd., Japan, Japanese Patent 2001348671 A2, 18 December 2001). The gold-plating bath contains $Au(NH_2CSNH_2)_2X$ (X = halo, NO_3) and a reducing agent selected from Na hypophosphite, thiourea, and tartaric acid. The bath requires no additional additives and plating can be performed in a stable manner.

7 Electronics

7.1 Electronic Conductive Characteristics of Devices Fabricated with 1,10-Decanedithiol and Gold Nanoparticles

The electronic conductive characteristics of composites made from 1,10-decanedithiol and gold nanoparticles were studied using a pressed pellet and with devices made from organic dithiols, gold nanoparticles, and *ca* 1 µm gap gold electrodes. T. Ogawa, K. Kobayashi, G. Masuda, T. Takase and S. Maeda, Precursory Research for Embryonic Science and Technology (PRESTO), Ehime, Japan, *Thin Solid Films*, 2001, **393**(1,2), 374-378, found that the I-V curve of the former pellet was Ohmic, and the temperature dependence ($\log\sigma$-1/T) of the conductance was not linear. In contrast, the micro-gap device gave a sigmoidal I-V curve. The activation energy for the latter was 6×10^{-3} eV which was one order smaller than the former pellet of 4×10^{-2} eV.

7.2 Effects of Metallization Characteristics on Gold Wire Bondability of Organic Printed Circuit Boards

Organic printed circuit boards (PCBs) with Au/Ni plates on bond pads are widely used in chip-on-board (COB), ball grid array (BGA), and chip-scale packages. These packages are interconnected using thermosonic gold wire bonding. The wire bond yield relies on the bondability of the Ni/Au pads. Several metallization parameters, including elemental composition, thickness, hardness, roughness, and surface contamination, affect the success of the solid state joining process. Various characterization and mechanical testing techniques were employed by J.K. Kim and B.P.L. Au of the Department of Mechanical Engineering, Hong Kong University of Science and Technology, Kowloon, Hong Kong, *J. Electron. Mater.*, 2001, **30**(8), 1001-1011, to evaluate these parameters for different metallization schemes with varying Ni and Au layer thicknesses. The pull force of Au wires was measured as a function of plasma treatment applied before wire bonding to clean the bond pads. Close correlations are established between metallization characteristics and wire bond quality.

7.3 Method for Manufacturing a Chip-Scale Package Having Copper Traces Selectively Plated with Gold

A patented method (D.S. Jeong, H.J. Sohn, and D.H. Lee, Samsung Electronics Co, Ltd., S. Korea, US Patent 6319828 B1, 20 November 2001) for manufacturing a chip-scale package consists of preparing a tape wiring board that includes a polyimide tape having top and bottom surfaces, copper traces formed on the bottom surface of the tape, a window formed in the tape to enable the copper traces to be connected to a semiconductor chip attached below the board, multiple connection holes formed in the tape to expose portions of the copper traces through it and define solder ball mounting pads, and an elastomer chip carrier attached to the bottom surface of the tape.

The method includes applying either a pre-flux or a cover sheet over the solder ball mounting pads. The pre-flux and the cover sheet each prevent the solder ball mounting pads being plated with gold. This, in turn, prevents the formation of intermetallic compounds in the solder balls so that the bond strength between the solder balls and a pad to which they attach is improved.

7.4 Preparation of CO_2 Lasers of the Macken Type

J.A. Macken invented CO_2 lasers with distributed gold catalyst in the discharge capillary wall. Y. Wang of the Southwest Jiaotong University, Chengdu, P.R. China, *Proc. SPIE-Int. Soc. Opt. Eng.*, 2001, **4274**(Laser Applications in Microelectronic and Optoelectronic Manufacturing VI), 448-451 consider that this type of laser has a bright future for applications. For studying its mechanism, two tubes of lasers, one with distributed gold catalyst, the other without, were prepared for comparison. Key techniques for preparing the new type of lasers is presented.

7.5 Microalloyed Gold Wire for Ball-Tip Bonding of Semiconductors in Electrical Circuits

The fine gold wire used for ball-tip electrical bonding of semiconductors is microalloyed with Ca 5-100, Gd 5-100, and Y 1-100 ppm by wt, up to 200 ppm total, optionally with rare-earth metal 1-100 ppm, and/or Mg, Ti, and/or Pb 1-100 ppm, up to 200 ppm total (H. Murai, S. Mitoma, T. Tokuyama and M. Motomura, Tanaka Denshi Kogyo K. K., Japan, European Patent 1160344 A1, 5 December 2001). The gold wire is inserted into a capillary mould, and heated to melt the tip to form a ball, and the ball tip is pressed against the electrode of semiconductor unit for electrical-circuit bonding. The gold wire is suitable for ball-tip bonding to the aluminium electrode film 0.5 µm thick. The typical microalloyed gold for the fine wire with ball tip size of 45-55 µm contains Ca 20, Gd 20, and Y 20 ppm (see also C.W. Corti, *Gold Bull.*, 1999, **32**, 39-47; C.H. Simons, L. Shräpler and G. Herlzlotz, *Gold Bull.*, 2000, **33** (3), 89-96).

7.6 Application of Super-Fine Gold Powder in Electronic Paste

Super-fine gold powders were prepared by dissolving gold in nitrohydrochloric acid, adding HCl, adding water, and reducing with hydrazine hydrate, oxalic acid, ascorbic acid, etc (H. Du, Kunming Institute of Precious Metals, P.R. China, *Dianzi Yuanjian Yu Cailiao*, 2001, **20**(4), 16-17) No.1 gold powder had spherical particles with an average size of 0.10-0.25 μm, and it was used in printing-type paste. No. 2 gold powder was mainly composed of flake-like particles with average size 1.5 μm, and it was used in welding paste.

8 Materials Science

8.1 Gold Nanoparticles, their Preparation, Application and Use for Decoration

Thiol-stabilized gold nanoparticles are claimed for decorative uses (*eg* coatings, metallic films, inks, and transfers) in a patent (P.T. Bishop, P.A. Marsh, B.J.S. Thiebaut and A.M. Wagland, Johnson Matthey plc, UK, WO Patent 2001068596 A1, 20 September 2001). Their preparation, coating compositions, and uses of gold nanoparticles are described. Using two-phase (water-toluene) reduction of $AuCl^{4-}$ by $NaBH_4$ in the presence of Aliquat 336 and HSC_6H_4-p-CMe_3, suspensions of 1-2.5 nm gold particles bearing a surface coating of thiol have been prepared. These can be applied to porcelain or china and fired to give a decoration.

8.2 The Colour of Nanodispersed Gold, Silver and Gold-Silver Solid Solutions in Glass Matrices

C.H. Ruscher and D. Speer of the Institut für Mineralogie, Universität Hannover, Germany, *CFI, Ceram. Forum Int.*, (2001), **78**(6), E41-E45, have prepared ceramic colours using a standard procedure of gold and silver basis compounds in a glass flux. The products were processed into decals on standard porcelain and fired in a temperature gradient between 760 and 860°C. The temperature treatment reveals small nanodispersed metal particles with average diameter between 27 and 43 nm. The purple colour of decals containing gold metal particles is due to Mie absorption peaked at *ca* 2.3 eV, which appears to be superimposed on interband transitions. Both the intensity of the Mie absorption and the band-band contribution decrease due to the increase of the crystal sizes with increasing firing temperature. The mixture of similar amounts of silver and gold based compounds shows a variation in their colour due to alloying. The related shift in the position of the Mie absorption peak indicates that gold is alloyed by Ag only up to *ca* 25% at the lower firing temperature. The silver content in the gold decreases with increasing firing temperature.

8.3 Crystallization Effect on Non-Linear Optical Response of Silicate Glass and Glass-Ceramics Containing Gold Nanoparticles

J. Sasai and K. Hirao of the Department of Materials Chemistry, Graduate School of Engineering, Kyoto University, Japan, *J. Non-Cryst. Solids*, 2001, **290**(1), 49-56, have prepared silicate glasses and glass-ceramics containing gold nanoparticles using a conventional melt-quenching method and subsequent two-step heat treatment processes. The relaxation time of nonlinear optical response of the gold nanoparticles was evaluated from femtosecond pump-probe measurements. The gold nanoparticles are precipitated through a heat treatment. A second heat treatment leads to the precipitation of Li_2SiO_3 nanocrystals on the gold nanoparticles. The relaxation of nonlinear optical response consists of two components; one is a fast relaxation within a few picoseconds, which originates from an electron-phonon coupling process, and the other is a slow relaxation due to a thermal diffusion of excess heat from nanoparticles to the glass matrix.

9 Medical and Dental

9.1 Gold-Coated NIR Stents in Porcine Coronary Arteries

When endovascular stents are altered to add functionality, *eg*, by adding radiopaque coatings, biocompatibility may suffer. E.R. Edelman, P. Seifert, A. Groothuis, A. Morss, D. Bornstein and C. Rogers, Harvard MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology, Cambridge, MA, USA, *Circulation*, 2001, **103**(3), 429-434, examined the vascular response in porcine coronary arteries to stainless steel gold-coated NIR stents (7-cell, Medinol, Inc). Stents, 9 and 16 mm in length, were left bare or coated with a 7 μm layer of gold. Physical and material effects were examined in four different gold-coated stent types, two at each length that either had the coating applied to the standard strut, *ie*, gold coated thicker than controls, or had the coating applied to thinned struts, *ie*, gold coated of the same thickness as control struts. Simple gold coating exacerbated intimal hyperplastic and inflammatory reactions over 28 days, but post-plating thermal processing smoothed the coating surface and negated the adverse tissue response to gold.

The relative amounts of base steel and gold coating and their resistances to expansion and collapse determined the extent of stent recoil. Gold coatings enhance the radiopacity of steel stents, but not without effects on vascular repair. Material effects predominate and can be abrogated by heating coated stents to alter surface finish and material purity. Clinical results may suffer unless consideration is given to material and physical effects of gold.

10 Metallurgy

10.1 Absence of Ferromagnetic Order in Ultrathin Rhodium Deposits Grown on Gold

Growth and magnetism of rhodium films in the thickness range between 0 and 6 monolayers on Au(111) were investigated at 30 and 300 K and after annealing at 300 K over a wide range of deposition temperatures using variable temperature ultra-high vacuum scanning tunnelling microscopy, Auger spectroscopy, and *in situ* Kerr effect measurements. I. Chado, F. Scheurer and J.P. Bucher, Institut de Physique et Chimie des Materiaux de Strasbourg Pasteur, CNRS, Université Louis Pasteur, Strasbourg, France, *Phys. Rev. B: Condens. Matter Mater. Phys*., 2001, **64**(9), 094410/1-094410/7, have shown that contrary to theoretical predictions, no ferromagnetism was detected by the Kerr effect, irrespective of the film thickness and the growth conditions. This disagreement may be due to invalid theoretical predictions, but it is most probably due to the experimental impossibility of growing a perfectly uniform film: surface intermixing in the first stage of growth is observed. Even upon low temperature deposition (at 30 K and above), a Rh-Au surface alloy forms, followed by a rhodium layer-by-layer growth.

10.2 Structure and Method for Bonding between a Gold Wire and an Aluminum Pad

This patented method (M. Ueda and K. Kuzuhara, Matsushita Electric Works, Ltd, Japan, Japanese Patent 2001284396 A2, 12 October 2001) involves sealing with a material containing bromine and involves Au_5Al_2 formation at the bonding. The bonding method may involve forming a palladium film on the pad to prevent the formation of Au_4Al. Secure bonding is obtained.

10.3 Bonding Pad Structure to Prevent Inter-Metal Dielectric Cracking and to Improve Bondability with Gold Wires

A process for forming a bond pad structure, with a roughened top surface topography, and used to improve the bondability of a gold wire to the underlying bond pad structure, has been patented by Y.-S. Huang, C.-C. Lin, C.-H. Lu and R.-L. Hwang of the Taiwan Semiconductor Manufacturing Company, Taiwan, US Patent, 6306750 B1, 23 October 2001. The process features the use of a W mesh pattern, formed in an IMD layer, and located underlying the bond pad structure, while overlying, and contacting, an underlying upper level, metal interconnect structure. The use of a W mesh pattern, in place of individual W studs, results in the creation of isolated islands, of IMED, reducing the bonding force, experienced by the IMD shapes, during the subsequent gold wire bonding procedure. In addition the W mesh pattern is formed via partial filling of a mesh pattern opening, in the IMD layer, resulting in an indented, or notched top surface. This in turn allows a roughened top surface, for the overlying bond pad structure, to be created, resulting in improved bondability of the gold wire, to the roughened top surface of the bond pad structure.

10.4 A New Gallide with a Three-Dimensional Gold-Gallium Network

D. Kussmann, R.D. Hoffmann and R. Pottgen, Department Chemie, Ludwig-Maximilians-Universität, Munchen, Germany, *Z. Anorg. Allg. Chem*., 2001, **627**(9), 2053-2056, report the synthesis of $Ca_3Au_{6.61}Ga_{4.39}$ by reacting the elements in a glassy carbon crucible under argon in a water-cooled sample chamber contained in a high-frequency furnace. The compound crystallizes with a new hexagonal structure type. This structure type consists of a remarkably complex three-dimensional $[Au_{6.61}Ga_{4.39}]$ network with significant Au-Au, Au-Ga, and Ga-Ga interactions. The calcium atoms are located within slightly distorted hexagonal channels of the Au-Ga network. The structural relations to the AlB_2- and Er_2RhSi_3-type structures are discussed.

10.5 A Dislocation-Based Description of Grain Boundary Dissociation in Gold.

High resolution transmission electron microscopy (HRTEM) observations and atomistic simulations of {111}/{121} facets in a gold 90° tilt boundary show the presence of a *ca* 10 Å wide layer with stacking faults distributed one to every three close-packed planes. D.L. Medlin, S.M. Foiles and D. Cohen, Sandia National Laboratories, Livermore, CA, USA, *Acta Mater*., 2001, **49**(18), 3689-3697, have examined this interfacial reconstruction, which forms the rhombohedral 9R stacking arrangement, and is similar to that found previously for near σ = 3{112} boundaries in low stacking fault energy metals. A general approach for partitioning grain boundary orientation into a set of Shockley partial dislocations is discussed and then this is applied to the {111}/{121} interface. The analysis explains both the distribution of faults and the geometry of the local plane bending and shows, further, that the 9R stacking occurs in both the σ= 3{112} and {111}/{121} interfaces due to the similar ratios of 30 and 90 degree Shockleys in both cases. The limitations of this description are discussed in relation to a 1/8[101] relaxation that is predicted by the atomistic simulations.

10.6 Melting Behaviour of Nanometre-Sized Gold Isomers

The melting behaviour of nanometre sized gold isomers has been studied by H.B. Liu, J.A. Ascencio, M. Perez-Alvarez and M.J. Yacaman, Instituto Nacional de Investigaciones Nucleares, Ocoyoacac, Estado de Mexico, *Surface Science*,

2001, **491**(1-2), 88-98, using a tight-binding potential with a second momentum approximation. The cases of cuboctahedra, icosahedra, Bagley decahedra, Marks decahedra and star-like decahedra were considered. The authors calculated the temperature dependence of the total energy and volume during melting and the melting point for different types and sizes of clusters. In addition, the structural evolutions of the nanosized clusters during the melting transition were monitored and revealed. The melting process has three characteristic time periods for the intermediate nanosized clusters. The whole process includes surface disordering and reordering, followed by surface melting and a final rapid overall melting. This is a new observation, which it is in contrast with previous reports where surface melting is the dominant step.

11 Refining

11.1 Application of meso Thermophilic Bacteria for the Oxidation of Gold Concentrate Containing Arsenopyrite and Pyrite

The application of meso thermophilic bacteria has been used to oxidatively leach gold concentrate containing high arsenopyrite and pyrite in Youanmi Mine of Australia. T. Zhu of the Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing, P.R. *China, Huangjin*, 2001, **22**(5), 27-30, reports that 120 tons of the concentrate has been treated per day since 1994, and the oxidation rate of As, pyrite, and total S was 90-95%, 25-30%, and 32%, respectively, and the cyanidation rate for gold, 97%.

11.2 A Review of the Flotation of Native Gold and Electrum

G.C. Allan and J.T. Woodcock, CSIRO Minerals, Clayton South, Australia, *Miner. Eng.*, 2001, **14**(9), 931-962, have reviewed this topic. Native gold and silver/gold electrum are naturally-occurring alloys containing gold and silver and a little copper. They are the most common and important forms of gold in ores. Their recovery by gravity concentration, cyanidation, or flotation from ores, typically containing 0.1-20 g/t gold is of great commercial importance.

This paper reviews the literature on their recovery by flotation. Little mention is made of the recovery of other gold minerals, but some comments are made on the flotation of host minerals (iron and base metal sulfides). Gold and electrum occur in a wide variety of ores in a wide spread of sizes ranging from large lumps (nuggets) to fine particles (0.1 μm) to even finer sizes below the resolution of the scanning electron microscopes.

The range of applicability of flotation is from about 200 μm flakes to 1 μm particles. Fundamental concepts of gold and electrum flotation are considered, including the possibility of collectorless flotation of the minerals.

Nine specific applications of native gold and electrum flotation to the treatment of gold-containing ores are identified and briefly discussed, as are other related topics.

11.3 Acidic Chlorination Leaching for Gold Recovery from Ore Concentrates or Industrial Wastes

In this patented method (R.L. Paul, J.M. de Sousa Rodrigues, S.P. O'Connell, G.O. Lewis, N. De Jager and G. Pattrick, Mintek, South Africa, WO Patent, 2001083835 A2, 8 November 2001) the gold in ore concentrate is recovered by: (a) leaching with aqueous HCl solution in the presence of chlorine gas to dissolve the gold and other metals; (b) separation of the loaded leach solution, especially by filtration and washing; and (c) selective gold precipitation from the leach solution, especially by reduction with SO_2 gas, Na metabisulfite or $FeSO_4$, or by cementation with copper or aluminium powder. The leached solids are suitable for additional treatment to recover silver values. The acidic leaching process is also suitable for electrochemical sludge or jewellery scrap containing >10% gold, optionally using bottled chlorine gas. The gold in the loaded solution is typically precipitated by reduction with $FeSO_4$ for 1-2 h, resulting in the final solution containing <2 mg Au/L. The precipitated Au powder has the nominal purity of 99.9%, and can be refined for 99.99% purity suitable for use in jewellery and coinage.

11.4 The Extraction of Gold from Plants and its Applications to Phytomining

Phytomining is the use of hyperaccumulating plants to extract a metal from soil with recovery of the metal from the biomass to return an economic profit. A.E. Lamb, C.W.N. Anderson and R.G. Haverkamp, Institute of Technology & Engineering, Massey University, Palmerston North, N.Z., *Chemistry in New Zealand*, 2001, **65**(2), 31-33, have examined the possible methods for recovering gold from plant material, including chemical reduction with and without solvent extraction, thermal reduction and copper electrodeposition.

Some progress was made with ascorbic acid as the chemical reductant. A solid phase was produced at the liquid-liquid interface after solvent extraction. The deposition reaction reduced the gold concentration in methyl iso-butyl ketone (MIBK) to less than 2 ppm, equating to 85% recovery, in 3.5 h. Copper electrodeposition also gave some promising results.

However, both methods require much more work before they are viable for scale-up (see also F.A. Msuya, R.R. Brooks and C.W.N. Anderson, *Gold Bull.*, 2000, **33**, 134-137.